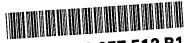


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- Thermosetting high solids coating composition of hydroxy-functional epoxies and anhydrides.
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#### Description

Background of the Invention Field of the Invention: The present invention is in the field of crosslinkable compositions comprising hydroxy-functional epoxy resins and anhydride curing agents. More specifically, the present invention relates to crosslinkable coating compositions having low volatile organic content which are particularly

Brief Description of the Prior Art: Color-plus-clear coating systems involving the application of a colored useful in color-plus-clear coating applications. or pigmented base coat to a substrate followed by the application of a transparent or clear top coat to the base coat are becoming increasingly popular as original finishes for automobiles. The color-plus-clear systems have outstanding gloss and distinctness of image, and the clear coat is particularly important for these properties. Illustratively, two-pack clear coat compositions comprising polyols such as polyester polyols, polyurethane polyols and acrylic polyols, and polyisocyanate curing agents give outstanding gloss

It is an object of the present invention to provide for a novel crosslinkable composition which provides for coatings which can be used in a wide variety of coatings applications. It is particularly the object of the and distinctness of image. present invention to provide a crosslinkable coating composition which can be formulated into a high solids coating composition with excellent adhesion, gloss and distinctness of image enabling the coating composition to be used as clear coats in a color-plus-clear coating system, particularly for use as an original finish for automobiles to provide remarkable appearance. It is furthermore the object of this invention to provide such a high solids crosslinkable composition having low volatile organic content (VOC).

Summary of the Invention In accordance with the foregoing, the present invention encompasses an improved process of applying a composite coating to a substrate, said process comprising applying to the substrate a colored filmforming composition to form a base coat, and applying to said base coat a clear film-forming composition to form a transparent top coat over the base coat; followed by heating the composite coating to a temperature sufficient to provide effective cure; the improvement comprising the clear and/or base coat containing a high solids solvent-based thermosetting composition comprising:

- (a) a low molecular weight hydroxy-functional polyepoxide, (b) a curing agent consisting essentially of an acid-anhydride comprising a monoanhydride,
- (c) a cure catalyst, said composition is characterized in that it is curable in the absence of a melamine

In the particularly preferred embodiment of this invention, the coating compositions typically contain cure catalysts which are tertiary amines or ammonium salts. The coating compositions of this embodiment have been found to be particularly suited to painting automobiles in the color-plus-clear mode to provide coatings having outstanding appearance and other desirable properties.

In this text, the terms molecular weight, solids content, volatile organic content (VOC) and appearance are defined as follows. The term "molecular weight" refers to a number average molecular weight as determined by gel permeation chromatography using a standard (such as polystyrene or glycol). Therefore, it is not the actual number average molecular weigh which is measured but a number average molecular

The solids (i.e., the non-volatile) content of a composition is determined by ASTM D-2369 testing weight which is relative to the standard. modified as follows: 0.3 grams of the composition is mixed with 5 milliliters of 1:1 mixture of acetone and tetrahydrofuran and heated at 110 °C. for 1 hour in a forced draft oven. The composition is then cooled in a desiccator, reweighed and the non-volatile content calculated. The percentage by weight of the composition

The term "sprayability" means the maximum concentration of solids at which the coating composition remaining is the solids content. can form a uniformly deposited coating, under normal spraying conditions, of say, temperature, pressure, and spray equipment design such as entails the use of an air suction gun operating at 60 psi with a No. 30 air cap. This maximum concentration is solvent dependent and usually occurs in a viscosity range of 20 to 80 and preferably at about 20 to 24 seconds with a No. 4 Ford cup at room temperature after thinning with a solvent such as a mixture of methyl amyl ketone and ethoxyethyl acetate. Above this maximum concentration, appearance of the coating as manifested by leveling and solvent popping typically becomes unacceptable.

The VOC is defined as the weight per volume of any compound of carbon which evaporates from a paint or related coating material under the specific conditions for the determination of the non-volatile content of that material. This does not include water which is volatile under the test conditions. Thus, the water content of the material undergoing analysis must be determined. To obtain the VOC of a sample, the non-volatile content, water content and the density of the material are determined. The VOC number is calculated by correcting the total organic volatile content for the water content and dividing by the volume of the paint corrected for the water content. The determination of the VOC is by ASTM D-3960 testing which entails heating the paint or related coating material at 110 °C. for 1 hour.

Appearance is defined in terms of distinctness of image (DOI) which is measured by a Dori-Gon Meter D47-6 manufactured by Hunter Laboratories.

## Detailed Description of the Invention

The coating compositions of this invention are high solids types. They have a sprayable solids content of about 45 percent or higher and preferably about 85 percent or higher. Also, the coating compositions have VOC of less than 3.6 and preferably less than 3 pounds per gallon, and down to about 1.8 pounds per gallon. As described more fully below, the components of the composition are selected on the basis that would result in high solids coating compositions having properties as described herein.

The hydroxy-functional polyepoxides useful herein are of low molecular weight and have epoxide equivalent weights of about 50 to 1000 and preferably about 100 to 300; a hydroxy equivalent weight of about 50 to 1000 and preferably 100 to 500. Typically, the hydroxy-functional polyepoxides contain more than 2 and preferably 3 or more epoxy groups per molecule, and at least one hydroxyl group per molecule. Typical but non-limiting examples of the hydroxy-functional polyepoxides are hydroxy-functional glycidyl ethers, hydroxy-functional glycidyl esters, hydroxy-functional glycidyl acrylic polymers, hydroxy-functional epoxidized oils, hydroxy-functional cycloaliphatic epoxies or mixture thereof.

Illustrative examples of the preferred glycidyl ethers are glycerol polyglycidyl ether having 3 epoxy groups; trimethylolpropane polyglycidyl ether having 3 epoxy groups; and diglycerol polyglycidyl ether having 3 epoxy groups, such as is available from Nagase America Corporation under the tradename

Illustrative examples of the hydroxy-functional glycidyl acrylic polymers are copolymers of ethylenically unsaturated monomers, one of which contains a glycidyl group and another which contains a hydroxyl group. The copolymers are prepared by free radical polymerization of the ethylenically unsaturated monomers. Examples of the ethylenically unsaturated monomers containing a glycidyl group can be a glycidyl acrylate, a glycidyl methacrylate, and an allyl glycidyl ether. Examples of ethylenically unsaturated monomers containing hydroxyl groups are hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, and the like. Other monomers that can be copolymerized with the above monomers can be alkyl esters of acrylic or methacrylic acid, e.g., ethyl acrylate, butyl acrylate or 2ethylhexyl acrylate, ethyl methacrylate, butyl methacrylate and the like; vinyl monomers such as styrene,

The anhydrides useful herein are of low molecular weight, and are typically polyacid anhydrides vinyl toluene and the like. comprising monoanhydrides. The molecular weight of the anhydrides can be in the range of about 100 to 500 and preferably about 100 to 200. Examples of the preferred monoanhydrides are alkyl hexahydrophthalic anhydrides wherein the alkyl group has up to 7 carbon atoms. A particularly preferred monoanhydride is methyl hexahydrophthalic anhydride. Other anhydrides that can be used herein are succinic anhydride, methyl succinic anhydride, dodecenyl succinic anhydride, octadecenyl succinic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride and the like. In the preferred embodiment of the invention, the polyacid anhydrides consisting essentially of monoanhydrides such as

The catalyst useful herein can be selected from the group consisting of tertiary amines such as dimethyldodecyl amine or dimethylethanol amine; onium compounds such as quaternary ammonium salt, e.g., tetrabutyl ammonium fluoride, tetrabutyl ammonium bromide, tetrabutyl ammonium hydroxide;

The proportion in which the components are employed is such as leads to the formation of gellable phosphonium salts and the like. compositions that can cure effectively. Hence, the equivalent ratio of the anhydride curing agent to the hydroxy-functional epoxy resins based on the anhydride to the hydroxyl group can be from about 0.5 to 20:1 and preferably 1 to 5:1. The equivalent ratio of the anhydride to the epoxy can be from about 0.3 to 5:1 and preferably about 0.5 to 2:1.

The aforedescribed components can be formulated into the claimed coating compositions which are typicaly solvent-based. The hydroxy-functional polyepoxide can be employed with only the anhydride as the curing agent to produce the claimed thermosetting coating compositions which can be heated to temperature sufficient to cure effectively. The cured coatings are hard and solvent resistant and can possess other desirable properties. Unlike the case of art-related coatings, other curing agents such as aminoplasts or isocyanates are not required to provide effective cure. Accordingly, the present invention can be said to encompass thermosetting high solids coating compositions consisting essentially of the hydroxy-functional polyepoxides, and anhydrides as curing agent therefor. It is, however, desired to point out that while the likes of aminoplasts are not required to effect cure, they can nonetheless be employed as coating additives

It is a distinct feature of the invention that the claimed thermosetting coating compositions are free of, or in less than the art-required curing amounts. substantially free of other curing agents, particularly melamine resins. This feature of the invention is all the more significant in the particularly preferred embodiment, wherein appearance is an important criterion. In this embodiment, the coating compositions typically contain cure catalysts such as tertiary amines or quaternary ammonium salts. Accordingly, in this embodiment the coating compositions consist essentially

In the coating formulation, additives such as ultraviolet light absorbers and/or stabilizers, flow control of the hydroxy-function polyepoxide, the anhydride and the cure catalyst. agents, antioxidants, plasticizers and the like can be employed. These additives can be employed in

amounts up to about 25 percent by weight based on the total resin weight. It is envisaged that the coating compositions of this invention can be practiced as multi-pack such as a two-pack coating compositions. For example, the hydroxy-functional polyepoxide and the cure catalyst can

The coating composition can be applied to a substrate by any of the conventional coating techniques be employed in one pack and the anhydride in another. such as brushing, spraying, dipping or flowing, but it is preferred that spray applications be used since this gives the best appearance. Any of the known spray techniques may be employed such as compressed air

spraying, electrostatic spraying and either manual or automatic methods. It is a distinct feature of the invention that the high solids thermosetting coating compositions of this invention display a surprisingly acceptable sag control at a film thickness of up to about 2 mils. Considering that coating compositions comprising low molecular weight components generally have sag control problems, it is indeed surprising that the instant coatings having low molecular weight components have the acceptable sag control. Thus, relatively lower amounts, if any at all, of sag control agents need to be added to the coating composition. Therefore, these coating compositions do not suffer a reduced solids content and poorer appearance, as is otherwise the case with art-related high solids compositions wherein sag

After application of the coating composition to the substrate, the coated substrate is heated to cure the coating. In the curing operation, solvents are driven off and the film-forming material of the top coat and/or control agents are added. of the base coat is crosslinked. The heating or curing operation is usually carried out at a temperature in the range of from 160-350 °F. (71-177 °C.) but if needed lower or higher temperatures may be used depending upon whether it is sufficient to activate any necessary crosslinking mechanisms. The thickness of the

The preferred coating compositions of the present invention, particularly those prepared with the coating is usually from about 1 to 5, preferably 1.2 to 3 mils. aliphatic polyepoxides, are used as clear coats for use in a color-plus-clear application. In a color-plus-clear application, a composite coating is applied to a substrate. The process comprises applying to the substrate a pigmented or colored film-forming composition to form a base coat and applying to the base coat a second film-forming composition to form a transparent top coat over the base coat.

The film-forming composition of the base coat can be any of the compositions useful in coating applications, particularly automotive applications in which the color-plus-clear coating applications are finding their most use. The film-forming composition conventionally comprises a resinous binder and is employed in combination with a pigment which acts as a colorant. Particularly useful resinous binders are acrylic polymers, polyesters including alkyds and polyurethanes. The resinous binder for the base coat can be an organic solvent-based material such as those described in U.S. Patent No. 4,220,679, note column 2, line 24, continuing through column 4, line 40. Also, water-based coating compositions such as those described in U.S. Patent No. 4,403,003 and U.S. Patent No. 4,147,679 can also be used as the binder in the base coat composition. The resinous binder for the base coat can also be the same as those of the present 55

As afore-stated, the base coat composition also contains pigments including metallic pigmentation to give it color. Examples of suitable pigmentations for the base coat are described in the aforementioned U.S. Patents Nos. 4,220,679; 4,403,003 and 4,147,679.

Optional ingredients in the base coat composition are those which are well known in the art of formulating surface coatings and include surfactants, flow control agents, thixotropic agents, fillers, antigassing agents, organic co-solvents, catalysts and other customary auxiliaries. Examples of these materials and suitable amounts are described in the aforementioned U.S. Patents Nos. 4,220,679; 4,403,003 and 4,147,679, but they are most often applied by spraying. The coating compositions can be applied by air spraying and electrostatic spraying in either manual or automatic methods which are preferred.

During application of the base coat to the substrate, a film of the base coat is formed on the substrate typically in a thickness of about 0.1 to 5 and preferably about 0.1 to 2 mils. After forming a film of the base coat on the substrate, solvent, that is, organic solvent and/or water, is driven out of the base coat film by heating or simply an air drying period before application of the clear coat. Preferably, the heating step will be for a short period of time sufficient to insure that the clear top coat composition can be applied to the base coat without the former dissolving the base coat composition, that is, "striking in". Suitable drying conditions will depend on the particular base coat composition, on the ambient humidity with certain waterbased compositions, but in general a drying time of from about 1 to 5 minutes at a temperature of about 80-175°F. (20-79°C.) will be adequate to insure that mixing of the two coats is minimized. At the same time, the base coat film is adequately wetted by the clear top coat composition so that satisfactory intercoat adhesion can be obtained. Also, more than one base coat and more than one top coat may be applied to develop optimum appearance. Usually between coats, the previously applied base coat or top coat is flashed, that is, exposed to ambient conditions for about 1 to 20 minutes.

The clear top coat composition is applied to the base coat by any of the conventional coating techniques mentioned above, although spray applications are typical. As mentioned above, the clear top coat is applied to the base coat via a wet-on-wet technique before the base coat has been cured. The two coatings are then heated to a temperature sufficient to cure and to conjointly harden both coating layers. Curing conditions such as described above can be used. In the preferred embodiments of the invention, the cured coatings are hard, solvent-resistance and possess the remarkable appearance and other desirable

Appearance of the color-plus-clear systems of this invention is remarkable. DOI measurement of the coating can range up to about 100. Overall, the combination of highly desirable properties of the claimed film properties. coatings, to wit, high solids, high sprayability, low VOC, acceptable sag control and excellent appearance,

The invention will be further defined by reference to the following examples. Unless otherwise indicated, markedly distinguishes the claimed coating over art-related coatings. all parts are by weight.

#### Example A

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This example illustrates a high solids thermosetting clear coating composition and the methods of preparing and using the same.

		Parts by Weight (grams)	Solids	
	Ingredients	Pack A	3.0	
5	TINUVIN 3281  Methyl ethyl ketone	16.5 1.0	1.0	
	TINUVIN 292 <sup>2</sup> Silicone fluid <sup>3</sup> Silicone fluid <sup>3</sup> stor calution in xylene)	1.0	0.1	
10	(10% 801001011	2.0	2.0	
	ARMEEN DM 12D4	48.0	48.0	
	DENACOL 421	4.0	1.0	
15	Cellulose acetate butyrate	Pack B	52.0	
20 25	Methylhexahydrophthalic anhydride  1 UV absorber available from Ciba Geigy Corp.  2 UV stabilizer available from Ciba Geigy Corp.  3 Available as DC 200 10CS from Dow Corning Co.  4 Dimethyldodecylamine available from Akzo Chemical Co.  5 Diglycerol polyglycidyl ether from Nagase America Corp.			
			ing them at a lov	

The above ingredients were formulated into a clear coating composition by mixing them at a low shear with good agitation. The resultant composition had a solids content of 87.3 percent measured at 110 °C. after 60 minutes, and a viscosity of 22 seconds measured with a number 4 Ford cup.

The clear coat was spray applied over a panel of steel substrates that had been electrocoated with UNI-PRIME® (which is a cationic electrodepositable composition available from PPG Industries, Inc.) and baked at 340 °F. (171 °C.) for 30 minutes. The electrocoated panels were spray painted with a base coat (available from ICI Limited as M-979) to a film thickness of 0.3 mil. The panels were then flashed for 3 minutes at 150 °F. (66 °C.), before the above clear coat was spray applied. The resultant color-plus-clear coat had a film thickness of 1.4 mils, DOI was 90, and Tukon hardness of 8.2.

This example illustrates a high solids thermosetting clear coating composition and the methods of Example B preparing and using the same.

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	a wallente	Parts by Weight (grams)	Solids		
	Ingredients	Pack A	_		
	1	3.0	3.0		
	TINUVIN 11301	3.0	3.0		
5	TINUVIN 292	3.0			
	guldene fluid	1.0	0.1		
	(10% solution in xylene)	4.0	1.0		
10	Cellulose acetate butyrate	3.0	3.0		
	ARMEEN DM 12D				
15	Epoxy/Hydroxy -functional	89.2	66.0		
	Acrylic Polymer 3	4.3	3.0		
	Polymeric acid	16.5			
	Methyl ethyl ketone	Pack B			
20	Methylhexahydrophthalic anh	ydride 34.0	34.0		
		rom Ciba Geigy Corp.			
	Methylhexanydrophera <sup>1</sup> UV absorber available from Ciba Geigy Corp. <sup>2</sup> The acrylic polymer was derived from 40% glycidyl methacrylate/15% butyl acrylate/25% methylmethacrylate/10%				
25	methacrylate/15% butyl	acrylate/25% methylmothes,			

CARDUARA E/Acrylic acid. (CARDUARA E which is an epoxy ester of Versatic acid, available from Shell Chemical Co. was herein reacted with acrylic acid).

<sup>3</sup>Polymeric acid derived from 2 moles of hexahydropthalic anhydride and 1 mole of 1,6-hexanediol.

The above ingredients were formulated into a clear coating composition by mixing them at a low shear with good agitation. The resultant composition had a solids content of 65.6 percent measured at 110 °C. after 60 minutes, and a viscosity of 22 seconds measured with a number 4 Ford cup.

The clear coating composition was spray applied over a panel of steel substrates that had been electrocoated with UNI-PRIME® (which is a cationic electodepositable compositon available from PPG Industries, Inc.) and baked at 340 °F. (171 °C.) for 30 minutes. The electrocoated panels were spray painted with a base coat (available from ICI Limited as M-979) to a film thickness of 0.3 mil. The panels were then flashed for 3 minutes at 150 °F. (66 °C.), before the above clear coat coating was composition spray applied. The resultant color-plus-clear coat had a film thickness of 1.4 mils, gloss (at 20 degree angle) was 86, DOI of 90, and Tukon hardness of 10.10.

This example further illustrates the clear coating composition of this invention and the methods of Example C making and using the same.

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	Ingredients	Parts by Weight (grams)	Solids
		Pack A	
		3.0	3.0
	TINUVIN 1130	3.0	3.0
5	TINUVIN 292	-	0.1
	Silicone fluid	1.0	
		3.0	3.0
	ARMEEN DM 12D	4.0	1.0
10	Cellulose acetate butyrate	4.3	3.0
	Polymeric acid	4.3	
	Hydroxy-functional glycidyl		
		104.0	60.3
15	acrylic polymer	Pack B	
			31.4
	Methylhexahydrophthalic anhy	ydride 31.4	-
	Same as in Example B.		
20	$^2$ Same as in Example B.		

The above ingredients were formulated by mixing them in the order indicated above at low shear with good agitation. The resultant composition had a determined solids content of about 70 percent (at 110 °C for 60 minutes) and viscosity of 31.5 seconds measured with a number 4 Ford cup.

The clear coating with spray applied wet-on-wet in a color-plus-clear mode as described in Example A. The resultant coating had a film thickness of 2 mils, DOI of 90 and Tukon hardness of 12.50.

#### Claims

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- 1. A process of applying a composite coating to a substrate by applying to the substrate a coloured filmforming composition to form a base coat and applying to said base coat a clear film-forming composition to form a transparent top coat over the base coat, followed by heating the composite to a temperature of 71° to 177°C, and effective curing of the composite coating,
  - using as the clear and/or base coating a solvent-based thermosetting coating composition having a
- solids content of at least 45 percent by weight, which comprises (a) hydroxy-functional polyepoxide selected from hydroxy-functional glycidyl ethers, hydroxy-functional glycidyl esters, hydroxy-functional glycidyl acrylic polymers and hydroxy-functional epoxidized
  - (b) a polycarboxylic acid monoanhydride curing agent, having a molecular weight in the range of 100 to 500, comprising succinic anhydride, methyl succinic anhydride, dodecenyl succinic anhydride, octadecenyl succinic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, a-d alkyl hexahydrophthalic anhydrides wherein the alkyl group has up
  - (c) a cure catalyst, wherein the quivalent ratio of anhydride groups to hydroxyl groups is 0.5:1 to 20:1 and the equivalent ratio of anhydride groups to epoxy groups is 0.3:1 to 5:1.
- 2. The process of claim 1, wherein the hydroxy-functional polyepoxide has an epoxide equivalent weight of 50 to 1000.
  - The process of claim 1, wherein the hydroxy-functional polyepoxide contains three or more epoxy
  - 4. The process of claim 1, wherein the hydroxy-functional polyepoxide is aliphatic.

- The process of claim 1, wherein the hydroxy-functional polyepoxide has a hydroxy equivalent of 50 to 1000.
- The process of claim 1, wherein the monoanhydride is methyl hexanhydrophthalic anhydride.
- 7. The process of claim 1, wherein the cure catalyst is a tertiary amine or a quaternary ammonium salt.
- The process of claim 1, wherein the thermosetting composition has a solids content of 45 to 85
- The process of claim 1, wherein the thermosetting composition has a VOC of 431 g/l (3.6 pounds per 10 gallon) or less.

#### Patentansprüche

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- 1. Verfahren zum Aufbringen einer Verbundbeschichtung auf einen Träger durch Aufbringen einer farbigen filmbildenden Zusammensetzung auf den Träger, um eine Grundschicht auszubilden, und Aufbringen einer klaren filmbildenden Zusammensetzung auf die Grundschicht, um auf der Grundschicht eine transparente Deckschicht auszubilden, anschließendes Erwärmen des Verbundes auf eine Temperatur von 71 ° bis 177 °C und wirksames Härten der Verbundbeschichtung,
  - Verwenden als die klare Schicht und/oder Grundschicht eine auf Lösemittel basierende wärmehärtbare Beschichtungszusammensetzung mit einem Feststoffgehalt von mindestens 45 Gew.-%, die enthält
  - (a) ein hydroxyfunktionelles Polyepoxid, ausgewählt aus hydroxyfunktionellen Glycidylethern, hydroxyfunktionellen Glycidylestern, hydroxyfunktionellen Glycidyl-Acrylpolymeren und hydroxyfunktionellen epoxidierten Ölen und Mischungen derselben,
    - (b) ein Polycarbonsäuremonoanhydrid mit einem Molekulargewicht im Bereich von 100 bis 500 als Härtungsmittel, enthaltend Bernsteinsäureanhydrid, Methylbernsteinsäureanhydrid, Dodecenylbernsteinsäureanhydrid, Octadecenylbernsteinsäureanhydrid, Phthalsäureanhydrid, Tetrahydrophthalsäureanhydrid, Methyltetrahydrophthalsäureanhydrid, a-d Alkylhexahydrophthalsäureanhydrid, in der die
    - (c) einen Härtungskatalysator, wobei das Äquivalentverhältnis von Anhydridgruppen zu Hydroxylgruppen von 0,5:1 bis 20:1 und das Äquivalentverhältnis von Anhydridgruppen zu Epoxygruppen 0,3:1 bis 5:1 beträgt.
- Verfahren nach Anspruch 1,

daß das hydroxyfunktionelle Polyepoxid ein Epoxidäquivalentgewicht von 50 bis 1000 aufweist.

- 3. Verfahren nach Anspruch 1,

daß das hydroxyfunktionelle Polyepoxid drei oder mehr Epoxygruppen enthält.

- Verfahren nach Anspruch 1, 4.
- dadurch gekennzeichnet, 45

daß das hydroxyfunktionelle Polyepoxid aliphatisch ist.

- Verfahren nach Anspruch 1,
- daß das hydroxyfunktionelle Polyepoxid ein Hydroxyäquivalent von 50 bis 1000 aufweist. 50
  - 6. Verfahren nach Anspruch 1,

dadurch gekennzeichnet, daß das Monoanhydrid Methylhexanhydrophthalsäureanhydrid ist.

- 7. Verfahren nach Anspruch 1,

daß der Härtungskatalysator ein tertiäres Amin oder ein quaternäres Ammoniumsalz ist.

- 8. Verfahren nach Anspruch 1, daß die wärmehärtbare Zusammensetzung einen Feststoffgehalt von 45 bis 85 % aufweist.
- 9. Verfahren nach Anspruch 1, daß die wärmehärtbare Zusammensetzung einen Gehalt von flüchtigen Bestandteilen (VOC) von 431 g/l (3,6 Pounds per Gallone) oder weniger aufweist.

#### Revendications 10

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- 1. Procédé d'application d'un revêtement composite sur un support, par application sur le support d'une composition filmogène colorée pour former une couche de base et application sur cette couche de base d'une composition filmogène transparente pour former une couche supérieure transparente sur la couche de base, suivie d'un chauffage du composite à une température de 71 à 177 °C, et du durcissement efficace du revêtement composite, caractérisé par l'utilisation, en tant que revêtement de base et/ou transparent, d'une composition de revêtement thermodurcissable à base de solvant et ayant une teneur en matière sèche d'au moins 45 % en poids, qui comprend
- (a) un polyépoxyde à fonctionnalité hydroxy choisi parmi des éthers glycidyliques à fonctionnalité hydroxy, des esters glycidyliques à fonctionnalité hydroxy, des polymères acryliques glycidyliques à fonctionnalité hydroxy et des huiles époxydées à fonctionnalité hydroxy, et des mélanges de ceux-20
- (b) un durcisseur de type monoanhydride d'acide polycarboxylique, ayant une masse moléculaire dans la plage de 100 à 500, comprenant l'anhydride succinique, l'anhydride méthylsuccinique, l'anhydride dodécénylsuccinique, l'anhydride octadécénylsuccinique, l'anhydride phtalique, l'anhydride tétrahydrophtalique, l'anhydride méthyltétrahydrophtalique, et des anhydrides alkylhexahydrophta-25 liques dans lesquels le groupe alkyle a jusqu'à 7 atomes de carbone,
  - (c) un catalyseur de durcissement, dans lequel le rapport d'équivalents des groupes anhydride aux groupes hydroxy va de 0,5:1 à 20:1 et le rapport d'équivalents des groupes anhydride aux groupes époxy va de 0,3:1 à 5:1.
  - Procédé selon la revendication 1, dans lequel le polyépoxyde à fonctionnalité hydroxy a un poids d'équivalent époxy allant de 50 à 1 000.
- 3. Procédé selon la revendication 1, dans lequel le polyépoxyde à fonctionnalité hydroxy contient 3 35 groupes époxy ou plus.
  - Procédé selon la revendication 1, dans lequel le polyépoxyde à fonctionnalité hydroxy est aliphatique.
- Procédé selon la revendication 1, dans lequel le polyépoxyde à fonctionnalité hydroxy a un équivalent 40 d'hydroxy allant de 50 à 1 000.
  - Procédé selon la revendication 1, dans lequel le monoanhydride est l'anhydride méthylhexahydrophtali-6.
  - Procédé selon la revendication 1, dans lequel la catalyseur de durcissement est une amine tertiaire ou un sel d'ammonium quaternaire.
- Procédé selon la revendication 1, dans lequel la composition thermodurcissable a une teneur en 8. matière sèche de 45 à 85 %. 50
  - 9. Procédé selon la revendication 1, dans lequel la composition thermodurcissable a une teneur en composés organiques volatils de 431 g/l (3,6 livres par gallon) ou moins.

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